OFFICE OF
RESEARCH AND DEVELOPMENT

May 29, 2019

Mr. Clark Friese, Assistant Commissioner
New Hampshire Department of Environmental Services (NHDES)
29 Hazen Drive
P.O. Box 95
Concord, New Hampshire 03301

Dear Mr. Friese:

I am pleased to provide the enclosed 5th report from our ongoing collaborative technical support to NHDES assisting with concerns over per- and polyfluorinated alkyl substance (PFAS) environmental contamination associated with manufacturing sites. This report is in response to your August 2017 request asking for laboratory assistance analyzing per- and PFAS in stock industrial dispersions and surfactants. The enclosed Report #5 provides non-targeted analysis results tentatively identifying various PFAS found in the dispersions and surfactants. We understand that these results are of interest to you in evaluating potential air emissions.

It is our understanding that this information was requested by NHDES to help in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analyses as they become available.

In this report, we do not interpret exposure or risk from these values. EPA does not currently have health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached reports indicate the presence (or lack) of PFAS in the dispersion and surfactant samples, no conclusions can be made related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and New Hampshire's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at watkins.tim@epa.gov or Tim Buckley at (919) 541-2454 or via email at buckley.timothy@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

CC: Meghan Cassidy, USEPA, Region 1
        Deb Szaro, USEPA, Region 1
        Jennifer McLain, USEPA OW
        Jessica Kramer, USEPA OW
        Mike Koerber, USEPA OAR
        Jeff Morris, USEPA OPPT
        Betsy Behl, USEPA, OW
        Andy Gillespie, USEPA, ORD
        Timothy Buckley, USEPA, ORD

PFAS Environmental Contamination Associated with Manufacturing Sites in New Hampshire

Laboratory Data Report #5: Non-Targeted PFAS Measurements in Commercial Dispersions and Surfactants

Background. The New Hampshire Department of Environmental Services (NHDES) in coordination with EPA Region 1 requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) in stock industrial dispersions and surfactants being used at a manufacturing site(s) within the State of New Hampshire. NHDES assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis. ORD's analysis and report team that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development analysis and report team.

Responsibility	Personnel
Laboratory chemistry	John Washington, Charlita Rosal, Mary Davis, Matthew Henderson, Brad Acrey, Mark Strynar, James McCord, Andy Lindstrom
Quality Assurance Review	Sania Tong Argao
Management coordination and review	Kate Sullivan, Brian Schumacher, Tim Buckley
Report Preparation	John Washington, Brian Schumacher, Tim Buckley

This 5th report includes non-targeted analysis results of commercial dispersions and surfactants that were collected by NHDES in August 2017 from stocks being used at an industrial site within New Hampshire. A total of 13 samples were collected. Samples 1 through 8 were labeled as "dispersions" and samples 9 through 13 were labeled as "surfactants." An additional 4 quality control (QC) laboratory blanks were analyzed with the 13 samples. The shipment was received by our Athens, GA lab on August 30, 2017 and analyzed under the direction of Dr. John Washington.

The current data report is intended to provide a simple representation and summary of laboratory results. Therefore, the description of methods, results and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed description of methods, results, quality assurance procedures, and statistical interpretation of the data. As study partners/collaborators, we anticipate that NHDES and Region 1 will assist in these reports and publications.

Methods in Brief. The PFAS reported here were extracted and analyzed according to methods documented within an approved Quality Assurance Project Plan (NERL, 2017). These methods are also generally described in Washington *et al.* (2014, 2015). Per- and polyfluoroalkyl substances (PFAS) were identified and quantified using a non-targeted analysis approach. Non-targeted analysis differs from targeted analysis in that chemical identification and quantification does not have the benefit of being based on a known standard for each compound. Accordingly, there is more uncertainty both in terms of identification and quantification for these non-targeted analytes.

In brief, the following methods of analysis were used. Each sample was shaken overnight to homogenize the sample. Aliquots of each sample were dispersed in methyl-tert-butyl-ether (MTBE). Fractions of these MTBE extracts were centrifuged to drop out solids and reserved for gas chromatography/mass spectrometry (GC/MS) analysis. Other fractions of these MTBE extracts were diluted in 60:40 acetonitrile:water (ACN/H$_2$O) and reserved for liquid chromatography/mass spectrometry (LC/MS) analysis. The GC/MS system used was an Agilent 7890B GCxGC coupled to a LECO Pegasus® TOF mass spectrometer providing low mass-resolution. The LC/MS instrument was a Waters Acquity ultra-performance liquid chromatograph (UPLC) coupled to a Waters Xevo G2-XS quadrupole time-of-flight (QToF) mass spectrometer providing high mass-resolution capability.

Non-targeted analysis provides two important measurements. The first is a tentative identification of PFAS compounds detected in the sample. PFAS are tentatively identified based on a combination of mass spectral data along with patterns of fragmentation compared to on-line and in-house mass-spectral libraries. Tentative identifications were determined for each sample and process blank. Process blanks are important for evaluating processing and/or solvent contamination that is not attributable to the samples. The second measurement is an indication of how much of the PFAS was present in the sample. The mass spectrometer detector provides quantitation as peak area counts. The peak area counts are proportional to the mass of PFAS in the sample. Since the sample and injection volume are held constant, the peak area counts are also proportional to concentration. However, without a standard, we are not able to derive a mass or concentration value. Accordingly, results are provided as peak area counts. It is important to emphasize that instrument response is highly variable among analytes and between samples. In the absence of quantitation based on known standards, and accounting for dilution ratios, results are considered semi-quantitative. For the GC/MS results, select analyte masses were extracted from the non-targeted analytical data set and reported as a "detect" when acceptable chromatographic peaks and spectra were evident. For the GC/MS results, we only determine PFAS presence/absence and do not provide any quantitation.

Summary of Results. Across all the dispersion/surfactant samples, we detected and tentatively identified 40 different PFAS. The likely identity of those PFAS and the samples where they were found is given in Table 2. We also provide a chemical reference ID to EPA's CompTox Chemicals Dashboard (U.S. EPA CompTox, 2019) where additional information about these chemicals can be found for the 27 PFAS that have been registered. The fact that 13 of these PFAS have not been registered is an indication of the novelty of our findings.

In Table 3 we report chromatographic peak area counts for the 40 PFAS identified in Table 2. Peak area counts are superimposed on a heat map where gradations in color reflect seven classifications of peak area from low (non-detect) to high (>100,000,000). The heat map is useful in showing the samples where PFAS was detected and their relative peak areas. The results reported are not corrected or adjusted for sample dilution that was required to prevent fouling of the instrument.

PFAS was detected in all the samples. However, the number of PFAS detected and their peak areas varied considerably. On the low end of the distribution, there were three samples (4, 8, and 13) where no PFAS was observed with peak areas greater than 2 times the blank (>2x blank). For the remaining samples, there was at least one PFAS that exceeded the 2x blank threshold and a peak area is reported. All other PFAS were either not detected or less than 2 times the maximum blank (<2x blank) as shown in Table 3. Sample 3 had the highest frequency of PFAS detection (20 of 40) whereas samples 10 and 11 included PFAS with the highest area counts observed of all the samples analyzed. These results contrast with what we have observed historically in analyzing commercial dispersions of legacy fluorotelomer-based polymers (FTPs) where numerous PFAS monomers at percent-level concentrations act as surfactants to keep the FTPs in suspension (Washington et al. 2014). We identified several non-PFAS components likely serving as formulation replacement for PFAS in these samples, but do not report them here. Examples of these non-fluorinated chemicals include the surfactants lauryl sulfate, glyceryl pentadecanoate, and dodecylbenzenesulfonic acid.

Sample 3 is also noteworthy because among the 20 PFAS present, several are in the PFAS series that have been previously identified in Char and Soil (ORD Technical Support to New Hampshire Report #2). The first of the PFAS are carboxylic acids that range from C4 to C18 (see compounds 28-35 on Table 1) that were tentatively identified as C6 to C20 in Report #2 where there is a single hydrogen substitution for fluorine. The hydrogenated polyfluorinated carboxylic acid (HPFCA) was identified based on mass spectral data including high resolution mass and fragmentation data leading to a high confidence level in its identification even in the absence of authentic standards. However, at present, the exact location of the hydrogen substitution or the presence/absence of branching cannot be clearly delineated. Therefore, a CAS number for this PFAS cannot be positively assigned. The second PFAS series in dispersion 3 was also identified previously in ORD Technical Support to New Hampshire Report #2 (see compound #'s 20-27). The tentative identification is a hydrogenated polyfluorinated sulfonic acid (HPFSA) series (Table 2) that ranges from C2 to C16 (tentatively identified as C4 to C18 in Report #2). As with the HPFCA series, there is a single hydrogen substitution for fluorine. We are continuing to investigate the presence of HPFCA and HPFSA in the dispersion, stack char, and soil as it relates to source attribution.

We identified volatile PFAS in four of the samples (9, 10, 11, and 13) as determined by GC/MS (Table 2, Compound #'s 36-39). The detection of volatile PFAS may be of relevance to air emissions.

In conclusion, in analyzing 13 dispersions/surfactants in use at manufacturing sites in NH, we have provided tentative identification of 40 PFAS including 13 that lack a record within EPA's CompTox Chemical Dashboard. PFAS compounds were identified in all 13 dispersions/surfactants with relative concentrations ranging from non-detect to likely percent levels. The identification of PFAS within stock dispersions/surfactants used at manufacturing sites in NH serve to inform NHDES on environmental surveillance and source attribution efforts.

Table 2: PFAS tentatively identified by non-targeted analysis in thirteen commercial dispersions or surfactants.

Compound #	Tentatively Identified Chemical Name	Chemical Reference ID in EPA's CompTox Chemicals Dashboard: https://comptox.epa.gov	Chemical Formula	Expected Mass (Daltons)	Dispersion/ Surfactant # where detected*	Comment Code
1	2-[3-(Difluoromethyl)-5-methyl-1H-pyrazol-1-yl]-N'-[(1Z)-3-methylcyclohexylidene]acetohydrazide	-	C14H2OF2N4O	298.1605	2, 7, 12	N, H
2	N-(3-Amino-2,2-difluoropropyl)-2-(4-benzyl-1-piperazinyl)acetamide	-	C16H24F2N4O	326.1918	1-5, 7-8, 10, 12-13	N, L
3	1,1,1,2,2,3,3,4,4,5,5-Undecafluoro-7-iodododecane	-	C12H14F11I	493.9964	All	N, H
4	Methyl N~2~-{[(2-methyl-2-propanyl)oxy]carbonyl}-N~6~-({[4-(trifluoromethyl)benzyl]oxy}carbonyl)-L-lysyl-L-lysinate	-	C27H41F3N4O7	590.2927	All	N, H
5	5:3Fluorotelomer carboxylate	DTXCID201012167	C8H5F11O2	342.0114	2-9, 11-13	N, H
6	7:3Fluorotelomer carboxylate	DTXCID6038297	C10H5F15O2	442.0050	12	N, H
7	9:3Fluorotelomer carboxylate	-	C12H5F19O2	541.9986	12	N, H
8	6:2Fluorotelomer unsaturated carboxylate	DTXCID701064818	C8H2F12O2	357.9863	9	N, H
9	6:2Fluorotelomer carboxylate	DTXCID40423370	C8H3F13O2	377.9925	12	N, H
10	6:2Fluorotelomer sulfonate	DTXCID7037711	C8H5F13O3S	427.9752	10	N, H
11	6:2Chloro Fluorotelomer sulfonate	-	C8H5ClF12O3S	443.9456	10	N, H
12	6:2 Fluorotelomer thioether amido sulfonate	DTXCID201079488	C15H18F13NO4S2	587.0470	2, 5-6, 10, 13	N, H
13	6:2Fluorotelomer sulfonylaminopropylammonioacetate	DTXCID2021284	C15H19F13N2O4S	570.0858	10	N, L
14	6:2 Perfluorooctyl phosphate	DTXCID00200745	C8H6F13O4P	443.9796	11	N, H
15	4:2 4:2 Diperfluorooctyl phosphate	-	C12H9F18O4P	589.9951	11	N, H
16	6:2 4:2 Diperfluorooctyl phosphate	DTXCID401032672	C14H9F22O4P	689.9887	11	N, H
17	6:2 6:2 Diperfluorooctyl phosphate	DTXCID80201210	C16H9F26O4P	789.9823	11	N, H
18	HFPO-DA (GenX)	DTXCID101021793	C6HF11O3	329.9750	6	N, H
19	Phenyl-HFPO Trimer	DTXCID301326034	C15H5F17O4	571.9916	12	N, L
	Hydro-polyfluoroalkylsulfonate series					
20	Hydro-polyfluoroethanesulfonate	DTXCID70387239	C2H2F4O3S	181.9661	3	N, H
21	Hydro-polyfluorobutanesulfonate	DTXCID801022285	C4H2F8O3S	281.9597	3	N, H

Compound #	Tentatively Identified Chemical Name	Chemical Reference ID in EPA's CompTox Chemicals Dashboard: https://comptox.epa.gov	Chemical Formula	Expected Mass (Daltons)	Dispersion/ Surfactant # where detected*	Comment Code
22	Hydro-polyfluorohexanesulfonate	-	C6H2F12O3S	381.9533	3	N, H
23	Hydro-polyfluorooctanesulfonate	-	C8H2F16O3S	481.9469	3	N, H
24	Hydro-polyfluorodecanesulfonate	-	C10H2F20O3S	581.9405	3	N, H
25	Hydro-polyfluorododecanesulfonate	-	C12H2F24O3S	681.9341	3	N, H
26	Hydro-polyfluorotetradecanesulfonate	-	C14H2F28O3S	781.9277	3	N, H
27	Hydro-polyfluorohexadecanesulfonate	DTXCID101325523	C16H2F32O3S	881.9213	3	N, H
	Hydro-polyfluoroalkylcarboxylate series					
28	Hydro-polyfluoroethanecarboxylate	DTXCID30278790	HC3F6COOH	195.9959	3	N, H
29	Hydro-polyfluorobutanecarboxylate	DTXCID501021757	HC5F10COOH	295.9895	3	N, H
30	Hydro-polyfluorohexanecarboxylate	DTXCID80516255	HC7F14COOH	395.9831	3	N, H
31	Hydro-polyfluorooctanecarboxylate	DTXCID30581670	HC9F18COOH	495.9767	3, 12	N, H
32	Hydro-polyfluorodecanecarboxylate	DTXCID101284965	HC11F22COOH	595.9704	3	N, H
33	Hydro-polyfluorododecanecarboxylate	DTXCID601284984	HC13F26COOH	695.9640	3	N, H
34	Hydro-polyfluorotetradecanecarboxylate	DTXCID901284971	HC15F30COOH	795.9576	3	N, H
35	Hydro-polyfluorohexadecanecarboxylate	-	HC17F34COOH	895.9512	3	N, H
36	6:2 Fluorotelomer alcohol	DTXCID3024572	C8H5F13O	364.0133	9, 10, 11, 13	V, H
37	6:2 Fluorotelomer acrylate	DTXCID7018840	C11H7F13O2	418.0238	9	V, H
38	6:2 Fluorotelomer iodide	DTXCID0027565	C8H4F13I	473.915	10, 11, 13	V, H
39	6:2 Fluorotelomer acetate	DTXCID301079481	C10H7F13O2	406.0238	10, 11, 13	V, H
40	Fluoro(heptafluoropropoxy)acetic acid	DTXCID40902493	C5H2F8O3	261.9876	2, 6	N, H

Comment Code: N = Non-volatile and measured by LC/MS, V =Volatile and measured by GC/MS, H = High confidence in identification, L = Lesser confidence in identification.

*Samples were diluted to bring the most abundant PFAS into the working range of the instrument. This dilution may have resulted in an inability to detect some PFAS in some samples.

Table 3. Detection and measurement of PFAS in dispersion and surfactant samples. Results are reported as peak area units. Table cells are color-coded to indicate detection and peak area class.

Compound #	Formula	Dispersion Sample Number								Surfactant Sample Number				
		1	2	3	4	5	6	7	8	9	10	11	12	13
1	C14H2OF2N4O		181,000					174,000					364,000	
2	C16H24F2N4O	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank		<2x Blank	<2x Blank		<2x Blank		139,000	<2x Blank
3	C12H14F11I	10,400	7,190	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	101,000	<2x Blank
4	C27H41F3N4O7	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	448,000	<2x Blank
5	C8H5F11O2		<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank	<2x Blank		<2x Blank	2,790	<2x Blank
6	C10H5F15O2												6,430	
7	C12H5F19O2												6,600	
8	C8H2F12O2									733				
9	C8H3F13O2												1,840	
10	C8H5F13O3S										1,470			
11	C8H5ClF12O3S										919			
12	C15H18F13NO4S2		73,700			21,100	485,000				2,460,000			<2x Blank
13	C15H19F13N2O4S										567			
14	C8H6F13O4P											203,000		
15	C12H9F18O4P											1,420		
16	C14H9F22O4P											141,000		
17	C16H9F26O4P											14,500,000		
18	C6HF11O3						432							
19	C15H5F17O4												2,710	
20	C2H2F4O3S			<2x Blank										
21	C4H2F8O3S			1,450										
22	C6H2F12O3S			7,630										
23	C8H2F16O3S			8,930										
24	C10H2F20O3S			8,620										
25	C12H2F24O3S			10,100										
26	C14H2F28O3S			12,000										
27	C16H2F32O3S			3,650										
28	HC3F6COOH			<2x Blank										

Compound #	Formula	Dispersion Sample Number								Surfactant Sample Number				
		1	2	3	4	5	6	7	8	9	10	11	12	13
29	HC5F10COOH			865										
30	HC7F14COOH			4,540										
31	HC9F18COOH			8,180										537	
32	HC11F22COOH			15,000										
33	HC13F26COOH			24,600										
34	HC15F30COOH			13,500										
35	HC17F34COOH			703										
40	C5H2F8O3		313				18,000							

Note: Compound numbers 36-39 listed in Table 2 are volatile PFAS identified by GC/MS but not quantified and are not included in this table.

LEGEND	
Color	Peak Area Category
	No Detection
	<2x Maximum Blank
	≥2x Maximum Blank to 30,000
	30,000 - 100,000
	100,001-400,000
	400,001 -1,000,000
	>1,000,000

References

National Exposure Research Laboratory (NERL), Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES), October 2, 2017.

Washington, J. W., T. M. Jenkins, K. Rankin and J. E. Naile (2015). "Decades-scale degradation of commercial, side-chain, fluorotelomer-based polymers in soils & water." Environmental Science & Technology 49(2): 915-923.

Washington, J. W., J. E. Naile, T. M. Jenkins and D. G. Lynch (2014). "Characterizing Fluorotelomer and Polyfluoroalkyl Substances in New and Aged Fluorotelomer-Based Polymers for Degradation Studies with GC/MS and LC/MS/MS." Environmental Science & Technology 48(10): 5762-5769.

U.S. EPA CompTox Chemicals Dashboard https://comptox.epa.gov/dashboard